Task 18

Fundamental and Applied Experimental Investigations of Corrosion of Steel by LBE under Controlled Conditions: Kinetics, Chemistry Morphology, and Surface Preparation

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BACKGROUND

This effort is a continuation of the work of Task 3 (see pages 10 and 11), and the same overview applies. Advanced nuclear processes such as the transmutation of nuclear waste, fast reactors, liquid-metal-cooled reactors, and spallation neutron sources require advanced materials systems to contain them. The required structural materials must be stable in the presence of non-moderating coolants. A prime candidate for such a coolant is Lead Bismuth Eutectic (LBE). Materials in these systems must be able to tolerate high neutron fluxes, high temperatures, and chemical corrosion. Unfortunately, LBE corrodes stainless steel.

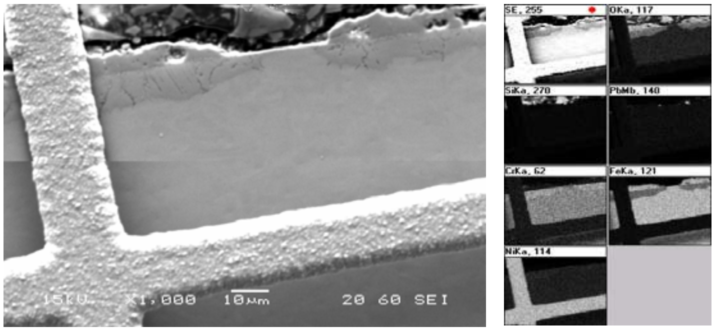
The corrosive behaviors of structural materials in LBE are not well understood. The Russians have over 80 reactor-years experience with LBE coolant in their Alpha-class submarine reactors. The Russians found that the presence of small amounts of oxygen in the LBE significantly reduced corrosion, but a fundamental understanding is incomplete. The formation and breakdown of protective (or non-protective) oxide layers in a steel/LBE is a key materials question.

RESEARCH OBJECTIVES AND METHODS

Samples of steel exposed to LBE were examined using various types of surface microscopy: Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX), X-ray Photoelectron Spectrometry (XPS) with sputter depth profiling (SDP), and Laser Raman Spectroscopy. The objectives are (1) to examine the morphology and composition of the oxide layer, its elemental and chemical composition, and its relation to the bulk material, (2) to probe the formation, nature, composition, breakdown, passivation, and healing of oxide layers on steel exposed to LBE, and (3) thereby gain insight into the fundamentals of corrosion of steel by LBE.

The following 8 activities were conducted:

- The UNLV group has continued collaborations with the LANL group, which has an LBE loop (“DELTA” loop). Samples of steel that were exposed to LBE at the DELTA loop at LANL were analyzed.
- Silicon has been proposed as a component to improve the corrosion resistance of steel in LBE systems. Si-containing steel that was exposed to LBE by Eric Loewen at INL was examined.
- A bay in the chemistry building, CHE 112C, was converted into the High Temperature Materials Experimental Facility (HTMEF).
- An experimental apparatus, the Liquid Metal Corrosion Experiment (LMCE) is being built.
- Gas phase experiments, using a tube furnace, has been started.
- An existing ion beam apparatus will be restarted to produce mass-selected ion beams. These will be used for isotopic labeling experiments for studying diffusion rates of iron, oxygen, nickel, and chromium atoms in steel matrices at elevated temperatures. Detection will be accomplished using the SIMS-TOF experiment at the EMSL laboratory at PNNL.
- A laser Raman experiment was designed to examine the chemical species present in oxide films produced in steel/LBE corrosion experiments.
- Corrosion of D-9 steel, which is a proprietary surface treatment, was studied.



D-9 shows failure of the thin oxide and formation of duplex oxide in localized patches. The iron moved outside the original metal surface to form Fe_3O_4 (as shown by Raman spectroscopy) and the chromium stayed in place to form an iron/chromium oxide which undercuts the thin oxide.

RESEARCH ACCOMPLISHMENTS

Approximately 250 DELTA loop samples were analyzed using SEM and EDAX. This was important to the LANL research group, which was having some issues controlling the crucial oxygen level in their DELTA loop.

The silicon-containing steel samples at INL were examined using SEM, XPS, and SDP. Samples with four different concentrations of silicon were examined. Silicon was found in the form of elemental silicon (in the metal), in the form of silica (SiO_2) at the bottom of the oxide layer, and silicates in the oxide. A layer of silica formed between the oxide and the bulk metal. The details were written up and published in the peer-reviewed *Journal of Nuclear Materials*.

Renovation of room CHE 112C into The High Temperature Materials Exposure Facility (HTMEF) was largely completed. This included renovating the floor, walls, air conditioning, and utilities. Experiments can now start in the HTMEF. The first two experiments will be the LMCE and the gas-phase experiments.

Construction continues on the Liquid Metal Corrosion Experiment (LMCE). This experiment will be placed in the HTMEF.

The first experimental results using the gas-phase experiment were obtained, using a quartz tube in a tube furnace, containing a steel sample and a copper/copper oxide pellet to determine the oxygen level.

The Raman experiment obtained its first results. The Raman technique allows determination of the chemical species (e.g., Fe_2O_3 or Fe_3O_4) while other techniques (XPS, EDAX) can only yield elemental composition (e.g., Fe and O are present but not what chemical species). Graduate student Brian Hosterman used the Raman experiment to demonstrate that the iron oxide in a sample exposed by the Russian collaborators was Fe_3O_4 and not Fe_2O_3.

Technical Summary

Investigations of steels samples exposed to LBE in a Russian test loop, as well as samples from other sources, are continuing.

It was found that very similar steels can show very different corrosion behavior in concert with different protective oxide morphology: slow corroding steels have a thin, high chromium surface layer similar to the initial oxide, while the faster corroding steels have a duplex oxide, magnetite above an iron-chromium oxide which is ~10x thicker than the thin protective oxide.

Inhibition of the conversion from protective thin oxide to less protective duplex oxide may lead to improved service life. Recently, an investigation of D9 steel, which has intermediate corrosion resistance, was finished. It was found that the oxide was primarily thin, with patches of duplex oxide.

The conversion from protective thin oxide to less protective duplex oxide seems to occur at localized sites. Further, the boundary between the chromium free magnetite layer and the chromium containing iron-chromium oxide is the same as the original metal surface – i.e. the chromium does not move nearly as rapidly as the iron does.

This means that the failure sites of the thin oxide in D9 are not healing to form thin oxide, in contrast with previous work on cold rolled 316 steel which did show healing to reform thin oxide. Control of the localized failure mode and understanding the healing mechanism may lead to improved corrosion resistance.

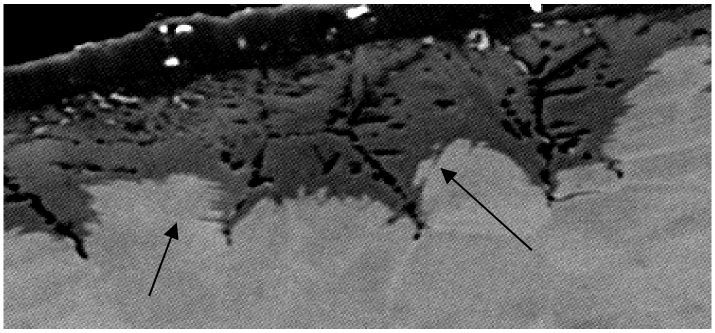
ACADEMIC YEAR HIGHLIGHTS

- A.L. Johnson, D. Koury, J. Welch, T. Ho, S. Sidle, C. Harland, B. Hosterman, U. Younas, L. Ma and J.W. Farley, “Spectroscopic and microscopic investigation of the corrosion of 316/316L stainless steel by lead–bismuth eutectic (LBE) at elevated temperatures. II. Initiation of duplex oxide formation in D-9 alloy,” presentation by Allen Johnson at the AFCI materials working group, March 2006, Santa Fe, NM

The migration channels for oxygen into and iron out of the iron-chromium oxide layer can be observed. Anisotropic etching of the underlying metal grains by the oxygen diffusing into the duplex oxide were noted, indicating some crystal planes seem to be more subject to oxidation than other planes. This opens another possible mechanism for improvement of oxidation resistance: If metal grains at the surface are oriented by shear between the underlying metal and the surface (by cold rolling, for example), the steel may become more resistant to formation of the thicker, non-resistant oxides.

FUTURE WORK

Development of the HTMEF and LMCE will continue, with experiments to follow. Gas phase experiments will provide useful baseline studies of low oxygen concentration corrosion of these systems. The Raman microscopy will allow in-situ characterization of the crystal phase of corrosion products in the oxide layers. Collaborative efforts with LANL will continue, with particular interest in new materials and new processes (the ion beam collaboration).



Atom probe image of etched D-9. Note high etch rate along grain boundaries and elsewhere. Arrows indicate evidence of oxidation along specific crystal planes in the metal

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